Sr$_2$Cu(PO$_4$)$_2$: A real material realization of the 1D nearest neighbor Heisenberg chain

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We present evidence that crystalline Sr$_2$Cu(PO$_4$)$_2$ is a nearly perfect one-dimensional (1D) spin-1/2 anti-ferromagnetic Heisenberg model (AHM) chain compound with nearest neighbor only exchange. We undertake a broad theoretical study of the magnetic properties of this compound using first principles (LDA, LDA+U calculations), exact diagonalization and Bethe-ansatz methodologies to decompose the individual magnetic contributions, quantify their effect, and fit to experimental data. We calculate that the conditions of one-dimensionality and short-ranged magnetic interactions are sufficiently fulfilled that Bethe's analytical solution should be applicable, opening up the possibility to explore effects beyond the infinite chain limit of the AHM Hamiltonian. We begin such an exploration by examining some extrinsic effects such as impurities and defects.

I. INTRODUCTION

Interest in magnetically low-dimensional systems began with the advent of quantum mechanics and the development of spin-spin interaction models to explain magnetic behavior. Though deceptively simple, early models such as Ising[1] or Heisenberg[2] cannot be solved for the general case, requiring either low spin or low spatial dimensionality to obtain analytical solutions. Exact solutions for some specific cases, such as Onsager's solution[3] to the two-dimensional (2D) Ising model or Bethe's solution[4] to the spatially one-dimensional (1D) s=1/2 Heisenberg chain, inspired general interest in the theoretical properties of magnetism in low dimensions, and resulted in a variety of predictions for exotic physical behaviors. Some of the most interesting properties to arise from the study of restricted-dimension magnets are due to the dramatic effect of quantum spin fluctuations[5]. These are intimately involved in the emergence of novel ground states and excitation spectra, and, in recent decades, have become a leading candidate as the pairing mechanism for electrons in quasi-2D high temperature superconductors[6], thus providing the field with a more practical aspect. Mermin and Wagner demonstrated[7] that strong spin fluctuations suppress magnetic long range order (LRO) until T=0 in isotropic spin systems in 1D and 2D, regardless of the interaction strength (exchange) between neighboring spins. Since real physical compounds are 3D by nature, the continuing effort to experimentally verify such predictions and probe the nature of 1D magnets is aimed at finding materials where magnetic interactions proceed predominantly along one direction. A measureable gauge of success or failure along these lines can be obtained through the ratio $k_B T_N/J_1$, which compares ordering temperature of a Néel state to the magnitude of exchange between neighboring spins. A perfectly 1D system would give $k_B T_N/J_1$ = 0. Additionally, experimentally observed behaviors should conform to theoretical predictions where the conditions of the model are met.

Recently, very low temperature measurements[8] on the spin-1/2 compound Sr$_2$Cu(PO$_4$)$_2$ identified the onset of magnetic LRO at T$_N$= 0.085 K, which, in combination with the extracted exchange constant, yields a ratio $k_B T_N/J_1$ = 6x10^{-4}. This is nearly a full order of magnitude less than the ratio[9] for prototype 1D magnet Sr$_2$CuO$_3$, which has $k_B T_N/J_1$ = 2.5x10^{-3}. We can estimate the remaining interchain coupling, J', by adopting an effective 3D chain model with $z_\perp$=4 nearest neighbor chains as in Ref. 10:

$$J' = \frac{3.046 k_B T_N}{k_{AFM} z_\perp \sqrt{\ln \frac{5.8 J_1}{k_B T_N} + 0.5 \ln \ln \frac{5.8 J_1}{k_B T_N}}} \approx 2.9 \times 10^{-2} \text{K},$$

(1)

where k_{AFM} is the magnitude of the AFM wavevector. All signs, therefore point to an extremely high degree of one-dimensionality that should justify the use of Bethe's exact analytical solution to the 1D spin-1/2 AHM in a wide temperature range $J' \ll k_B T$, provided that indeed *only nearest-neighbor* interactions are present. Previous studies[11] have shown that this condition is not satisfactorily fulfilled by the leading 1D spin-1/2 AHM candidate, Sr$_2$CuO$_3$. For completeness, another candidate for a 1D-AHM system should be mentioned: the linear charge transfer salt [3,3'-dimethyl-2,2'-thiazolinocyanine]-TCNQ[12,13].

Here, we undertake an extensive theoretical analysis of Sr$_2$Cu(PO$_4$)$_2$, employing first principles density functional theory calculations, an exact diagonalization scheme, and finally, a Bethe-Ansatz derived expression for the magnetic susceptibility fit to experimental data. Our results are in remarkable agreement with one another and with experimental observations. We show that Sr$_2$Cu(PO$_4$)$_2$ is indeed extremely 1D and that furthermore, the second-neighbor interactions are vanishingly small, eliminating any complications due to in-chain frustration. We claim, therefore, that this compound is the best realization of a nearest-neighbor only Heisenberg spin 1/2 chain known to date and will likely be a valuable tool for extracting intrinsic effects be-
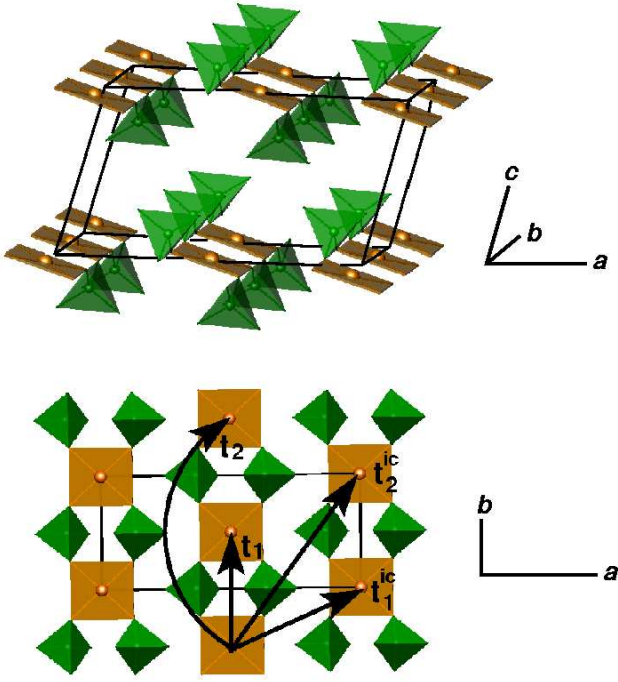
FIG. 1: (Color online) *Upper panel* The structure of $Sr_2Cu(PO_4)_2$, showing the isolated CuO_4 plaquettes as squares with O ions located at the corners, and the PO_4 units as tetrahedra with P located in the center. *Lower panel* A top view of the spin chain plane with the various hopping paths labelled. Hopping to the nearest out-of-plane neighbor, $t_\perp$, is not shown.

yond the Bethe-ansatz *i.e.* effects not contained in the Heisenberg Hamiltonian, such as Dzyaloshinsky-Moriya interactions[14], ring exchange processes, or spin-lattice coupling effects. Additionally, extrinisic effects due to sample imperfections such as defects, magnetic impurities or the presence of alternate phases can be quantitatively explored, and we make a preliminary investigation of some of them.

II. FIRST PRINCIPLES AND TIGHT-BINDING

First principles density functional theory (DFT) band-structure calculations were performed using a full-potential local orbital code, FPLO[15], with the following valence states: Sr (4s,4p,4d,5s,5p), Cu (3s,3p,3d,4s,4p), P (2s,2p,3s,3p,3d), O (2s,2p,3d). The structure, lattice constants, and atomic positions (see Fig. 1) were taken from experiment[16,17], $a = 11.515$ Å, $b = 5.075$ Å, $c = 6.5748$ Å. $Sr_2Cu(PO_4)_2$ and isostructural $Ba_2Cu(PO_4)_2$, which we calculate as a comparison material, are composed of isolated CuO_4 plaquettes surrounded by PO_4 tetrahedra. The plaquettes are spaced evenly along the b axis, forming chains that are staggered with respect to one another in the a crystal direction. The planar

CuO_4 units are tilted with respect to the $a - b$ crystal plane. Based on the geometry of these two systems, we enumerate five specific interactions between plaquettes, and therefore between spins localized to these plaquettes, that may be necessary to describe the electronic and magnetic structures. These interactions are labelled in Fig. 1 as various hopping parameters to be later included in a tight-binding model.

The paramagnetic band structure of $Sr_2Cu(PO_4)_2$ (Fig. 2) shows a single, isolated, half-filled band, derived predominantly from the Cu $3d_{x^2-y^2}$-O $2p_\sigma$ molecular plaquette orbital, crossing the Fermi energy. In reality, the system is antiferromagnetic (AFM) and insulating, but we will follow the standard procedure of importing hopping parameters from the "uncorrelated" paramagnetic system to the Hubbard model which then maps onto the Heisenberg model. Magnetism and correlation effects can also be added at the DFT level with, as we will show, very consistent results. The 1D character of the system is qualitatively obvious from the nearly dispersionless bands in directions perpendicular to the magnetic chains (S-Y and Γ-Z) and from the characteristic logarithmic divergences in the density of states (DOS) near the band edges. To quantitatively compare microscopic magnetic interactions, we fit a tight-binding (TB) model to our paramagnetic band structure and calculated the individual exchange constants between various CuO_4 plaquette spins using $J_{ij} = 4t_{ij}^2/U_{eff}$ with U_{eff}=4.5 eV.
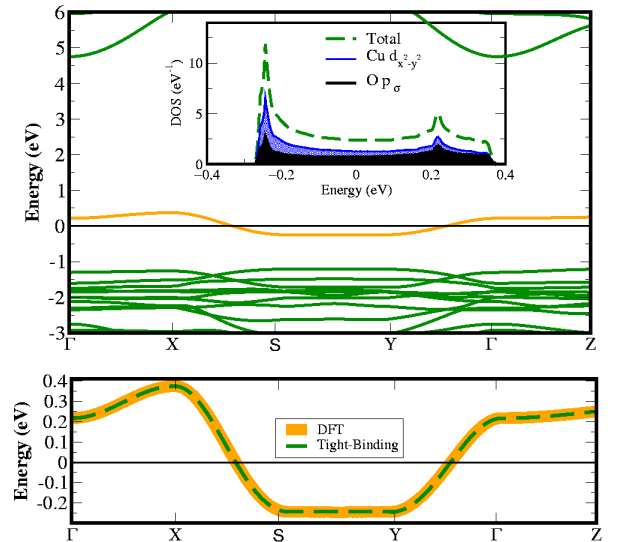

FIG. 2: (color online) The bandstructure of $Sr_2Cu(PO_4)_2$, showing the single metallic band well separated from all others. The $X - S$ and $Y - \Gamma$ directions are along the magnetic chain, while the $S - Y$ and $\Gamma - Z$ directions are perpendicular to the chain. The inset shows the total and orbitally resolved DOS for the single band. In the lower panel, a blow-up of this band is shown with tight-binding eigenvalues superimposed to show the remarkable reproduction of the dispersion.

We find this to be a reasonable choice for U_{eff} because of poor screening in this geometry and because of the small inter-plaquette repulsion. The hopping parameters included in the model are shown schematically in Fig. 1 with the numerical values and derived superexchange constants given in Table I. The resulting TB dispersion, which uses only 5 fitting parameters, is indistinguishable from the full-potential calculation (Fig. 2 lower panel), indicating that further interactions can be safely ignored. The ratio of the strongest in-chain coupling to the strongest interchain coupling is $J_1/J_1^{ic} \sim 70$ and the ratio of first to second neighbor in-chain coupling is $J_1/J_2 \sim 700$ for $Sr_2Cu(PO_4)_2$. Identical calculations based on the band structure of $Ba_2Cu(PO_4)_2$ (not shown) yield similar results with somewhat more inter-chain coupling but less second neighbor in-chain coupling. Both systems can therefore be considered as strongly one-dimensional, with $Ba_2Cu(PO_4)_2$ slightly less so. Naturally, the choice of U_{eff} is simply a best estimation and results for J will vary slightly with this choice, while the ratios will remain constant.

TABLE I: Tight-binding hopping parameters (in units of meV) and derived exchange constants (in units of K) for $A_2Cu(PO_4)_2$, A=Sr,Ba. See Fig. 1 for the relationship of the hopping parameters to the structure.

(meV)	t_1	t_2	t_1^{ic}	t_2^{ic}	$t_\perp$
Sr	135	5.1	16.3	3.4	1.4
Ba	122	0.9	10.3	4.7	1.8

(K)	J_1	J_2	J_1^{ic}	J_2^{ic}	$J_\perp$
Sr	187	0.268	2.7	0.119	0.02
Ba	154	0.008	1.09	0.228	0.03

The energy difference between FM and AFM ordered spin configurations can be calculated using the local spin density approximation (LSDA)[18] which allows for separate spin-up and spin-down densities. Since the LSDA is known to badly underestimate the onsite Coulomb interaction in localized systems, we applied the LSDA+U methodology to better account for the correlated Cu $3d$-orbitals, using the fully localized limit scheme[19] to correct for double-counting terms. We map a classical Néel state and a classical ferromagnetic state onto the Heisenberg spin model, including only 1D nearest neighbor interactions. Comparing the resulting model energy difference to the LDA energy difference between FM and AFM states (per spin), we derive an effective exchange constant, J_{eff}, in the following way:

$$H = \sum_{i,j} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j; \quad E_{FM}-E_{AFM} = 2J_{eff}|s|^2, \quad s = 1/2, \tag{2}$$

As expected, the energy difference, and therefore J_{eff}, decreases as U_d (not to be confused with the considerably smaller one-band parameter U_{eff} that contains O

$2p$ contributions in addition to Cu $3d$) increasingly localizes the Cu $3d$ electrons. For a range of U_d between 6 eV and 9 eV, we find that J_{eff} varies from 261 K to 160 K. Since U_d is a local quantity and since the Cu-O bond distance in $Sr_2Cu(PO_4)_2$ is only 1% different than in the plaquettes of the widely studied high T_c precursor systems, we adopt the commonly used value of $U_d = 8$ eV. This corresponds to a value of 190 K for J_{eff}. Note that since the LSDA (and LSDA+U) energy differences include contributions from *all* exchange processes in the system, J_{eff} cannot in general be considered as either purely superexchange or purely 1D. However, comparison with the individual superexchange parameters derived from the TB fit shows that both assumptions, in this case, are quite valid. The nearest neighbor in-chain TB exchange constant has a value $J_1 = 187$ K, in exceptional agreement with the J_{eff} value of 190 K, indicating that the next-nearest neighbor interactions, FM exchange processes and residual 2D and 3D interactions must therefore be extremely small. Of course both values can be made to vary somewhat by choosing U_d and U_{eff} differently, thus affecting the agreement as well. We expect that our calculated value of J will be larger than the experimental value, as it is well known that the band dispersion from which we derive t and subsequently J is generally exaggerated by the LDA. Indeed, the experimentally derived value of J is 143 K, in good but not perfect agreement with our calculations. We emphasize that any renormalization of the hopping parameters stemming from effects outside the LDA will cancel in the ratio (J_1/J_2) so that the precise calculated value of J has, in any case, no bearing on the establishment of the compound's pronounced magnetic one-dimensionality and short-ranged magnetic interactions that are the primary aim of our first principles study.

III. EXACT DIAGONALIZATION

We perform an exact diagonalization calculation using ten sites along two staggered AFM magnetic chains (20 sites total) for calculating thermodynamic properties such as specific heat and magnetic susceptibility, and using 36 total sites for obtaining the ground state properties. We compare calculations including the three largest exchange interactions, J_1, J_2 and J_{ic}^1, as listed in Table I, to calculations using only J_1. Since in our model each chain has only one neighboring chain, we also perform a calculation in which J_{ic}^1 is doubled to account for the existence, in reality, of two neighboring chains. In the case of specific heat, there is no discernable difference between any of the three curves using these different parameter sets. For the calculation of χ, the curves are identical for the majority of the temperature range explored ($0 < k_bT/J_1 < 3$), but a barely visible difference occurs near the peak of the curve (see Fig. 3). The maximal difference occurring between two curves is 0.9%, at about $k_BT/J_1=0.65$. The ground state calculations of
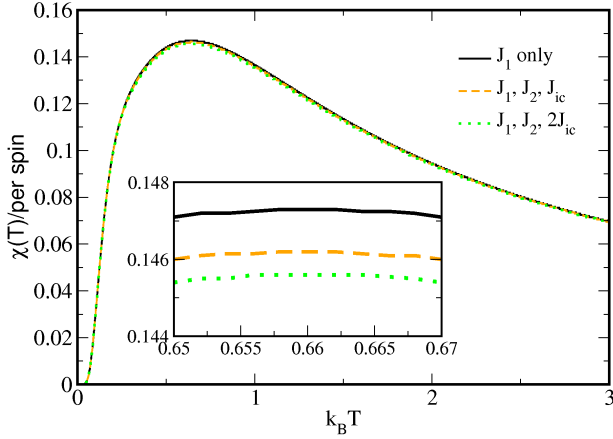
FIG. 3: A 20 site exact diagonalization calculation of the susceptibility per spin of $Sr_2Cu(PO_4)_2$. The inset shows a blow-up of the region where the curves have the greatest discrepancy - 0.9%. Curves for the ground state correlation of spins and for the specific heat per spin show even less deviation.
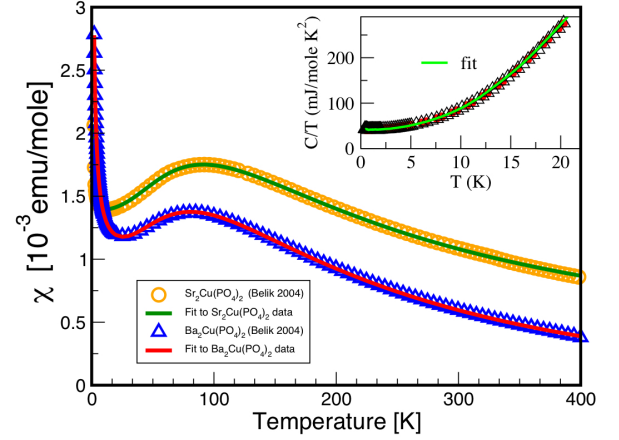

FIG. 4: Bethe-Ansatz fits to experimental data with corrections for broken chains, impurity phases, and domain boundaries. Note the consistency of the exchange parameter vs. the wide spread in values for the chain length.

the spin-spin correlation, $\langle S_i \cdot S_j \rangle$ are again completely indistinguishable. Obviously, more distant and weaker interactions, such as J_{ic}^2 and $J_\perp$ will have even less of an effect. From this we conclude that $Sr_2Cu(PO_4)_2$ is essentially free of magnetic interactions beyond the first neighbor and is an ideal candidate for Bethe-ansatz calculations, which we now discuss.

TABLE II: The collected results of fits to different sets of $\chi(T)$ data for $Sr_2Cu(PO_4)_4$ and $Ba_2Cu(PO_4)_4$.

$Sr_2Cu(PO_4)_2$	J(K)	N	g
Belik[16]	144.9	114	2.713
Belik[8]	143.9	337.7	2.154
Nath[23]	152.6	5	1.952

$Ba_2Cu(PO_4)_2$	J(K)	N	g
Belik[16]	131.8	48	2.073
Nath[23]	140.1	5	2.041

IV. COMPARISON WITH EXPERIMENT

The basic theory for non-periodic, open AHM chains was worked out by Furusaki and Hikihara[20] (FH) and also by Zvyagin and Makarova[21] (ZM). FH considered a half-infinite chain with *one* free chain end applying bosonization theory whereas ZM considered finite even-membered chains on the basis of a rigorous theory based on the Bethe ansatz. Both approaches result, at low temperature, in a chain length $(L = Na)$ dependent diverging contribution to the total magnetic susceptibility $\chi \propto 1/NT \ln(T_0 J_1)$ and to the linear coefficient in the specific heat $\gamma = C_p/T \propto 1/NT \ln^\beta(T_0 J_1/T)$, with $\beta = 2, 4$ in the FH and ZM theory, respectively. Since a real chain has two ends we multiplied the FH expressions by a factor of 2. ZM calculated further logarithmic corrections which we adopted here to be valid for the FH case, too. Then within both approaches we arrive finally at the same expression for the chain end contributions to χ (up to a factor of 3/4). For the logarithmic constant T_0 we used the same value 5.696 as proposed by Johnston *et al.* in the fit expression (fit2) for the bulk susceptibility[22], similarly to 5.8 used in Eq. (1). In the shown and described fits we have adopted the formalism of FH, modified as described above, for both C/T and χ.

We fit to both susceptibility and specific heat to data taken on the same sample[16], additionally using data from a later sample[23] for which only χ data was available. The fit quality for specific heat and susceptibility are very similar; results for the latter are shown in Fig. 4. We get very good fits throughout the entire temperature range and find a reasonably consistent value for the exchange parameter, J, despite fitting to samples of different qualities and to two different measurements (C/T and χ). It is worth noting that the exchange parameter derived from fitting to C/T using the data of Ref. 16 yields an exchange parameter of J=134.4 K, which is somewhat less than the value derived from fitting to $\chi(T)$ using the *same* sample. This is likely caused by non-magnetic impurity contributions (not accounted for in our model) that affect the specific heat but not the susceptibility at low temperatures. Since the magnetic component of C is $\propto 1/J$, ignoring the non-magnetic contribution overestimates this term and therefore underestimates the exchange. Unlike the exchange and g values, the chain length parameter, N, varies widely between samples. While this is expected for samples of different

quality, the variation is surprisinly high and, more importantly, the chain lengths resulting from our fits are far too small to justify the use of the open chain theories that we have employed at very low temperatures. With chain lengths of this order, the low temperature region will be completely dominated by broken chain physics that requires different, and as-of-yet undeveloped, formalism. Having fit throughout a large temperature range, including regions where broken chain physics is inoperative, we feel that the extracted exchange constant, J ≈ 145 K, is nonetheless relevant - a belief that is supported by its consistency between fits and its similarity to the experimentally measured value.

V. DISCUSSION

The application of a variety of theoretical techniques to the problem of magnetism in $Sr_2Cu(PO_4)_2$ convincingly demonstrates that the ideal compound is highly one-dimensional. The high degree of one-dimensionality can be traced back to its unusual isolated CuO_4 plaquette geometry. Instead of edge- or corner- shared plaquettes such as are common in other quasi-1D compounds[24,25], each Cu ion in $Sr_2Cu(PO_4)_2$ is surrounded by four O ions not shared by any other Cu ion. This construction virtually eliminates the second neighbor in-chain coupling that prevents edge-shared compounds such as Li_2CuO_2 from being described via a simple nearest neighbor Heisenberg model[26,27]. Corner shared cuprates such as Sr_2CuO_3 have far smaller second neighbor interactions[9], of the order $J_1/J_2 \sim 15$, and yet, these must be taken into account to get good agreement between model calculations and experiment[11]. The structure of $Sr_2Cu(PO_4)_2$ along the chain is that of an edge shared chain compound with every other unit missing. Conceptualized in this way, one can make a correspondence between exchange constants in a edge-shared (*es*) system and those in the isolated square plaquette (*sp*) geometry: $J_2^{es} \rightarrow J_1^{sp}$, and $J_4^{es} \rightarrow J_2^{sp}$. Since J_4^{es} is known to be vanishingly small in the edge-shared geometry, it is clear that the second neighbor interactions in the square plaquette geometry can be expected to be negligible. This may provide some directional guidance in the search for new one-dimensional compounds: the isolated plaquette arrangement appears to be superior to the more common edge- or corner-shared structures such that synthesis of new compounds with this geometry may prove to be profitable. The tilting of the out-of-chain plaquettes with respect to one another further suppresses the inter-chain coupling. The staggering of plaquettes in neighboring chains slightly increases the distance between spins, but more importantly, gives rise to frustration. As each chain is antiferromagnetically aligned by the (relatively) strong first neighbor coupling, a given spin finds itself surrounded by four interchain neighbors, two aligned in one direction and two in the other. These staggered, frustrated chains are more decoupled from one another than they would be in another arrangement, *e.g.* a ladder configuration.

Provided that $Sr_2Cu(PO_4)_2$ is stoichiometric and largely defect-free, it is clear that this compound represents the most 1D AHM chain so far investigated. These conditions are, unfortunately, not reasonably fulfilled by current samples. It is interesting in this context to consider the mechanism by which the compound eventually achieves LRO (at $T_N = 0.085$ K): is it truly the result of residual third dimension interactions? Significantly, the phenomenologically estimated averaged interchain interaction from Eq. 1 is of the same order as the calculated $J_\perp^1$, rather than J_{ic}^1. Fluctuation induced "order by disorder" coupling could be responsible for the strong reduction of two orders of magnitude within the frustrated plane. On the other hand, the interchain couplings are in general phenomenally small as calculated by DFT methods and even so are likely exaggerated. One alternative explanation is that in a system with many broken chains, there will be some number of chains containing an odd number of spins, with each such chain carrying one uncompensated spin-1/2 electron. The relationship of the uncompensated spins to one another is not defined by any of our methods and a long range ordering of these is not out of the question. It would be interesting to see if the ordering temperature remains constant with sample quality. Another point to be addressed in the future is the issue of spin-lattice coupling. The Heisenberg model itself assumes perfect isotropy in spin-space and we have not included any relativistic (spin-orbit) interactions in our first principles calculations. The neglect of these is seemingly justified by the extremely small field (H= 4mT) at which the spin-flop transition occurs[8], but the smallness of this field itself is unusual and a cause for further investigation. All of these facts point to the high desirability of better samples that can be used to disentangle true "dimensionality" effects from behaviors due to crystal imperfections. Although the investigation of true Heisenberg physics is currently limited by sample quality issues, $Sr_2Cu(PO_4)_2$ is theoretically, and potentially experimentally, the best example of a magnetically 1D crystal yet studied.

VI. CONCLUSION

We have shown that the isolated CuO_4 plaquette geometry of $Sr_2Cu(PO_4)_2$ gives rise to a nearly perfect 1D spin-1/2 nearest neighbor only system. We find a ratio $k_B T_N/J_1 = 6 \times 10^{-4}$, in good agreement with experimental finding and show that secondary interactions (2D,3D and next-nearest neighbor) are negligible in terms of calculated thermodynamic properties. Using the Bethe-ansatz solution to the Heisenberg Hamiltonian along with additional terms to correct for extrinsic non-crystalline effects, we fit the data over a large temperature range and derive an exchange parameter of 145 ± 5 K that is consistent between samples and between fitting choices. We find that sample quality, particularly the existence of

numerous broken chains, currently prohibits experimental observation of true spin-1/2 AHM physics. However, $Sr_2Cu(PO_4)_2$ is truly intrinsically perfectly 1D with only one exchange parameter, and as better and better methods of generating the compound emerge, effects beyond Bethe-ansatz can be probed experimentally.

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